

# Chapter 3

## Gas Adsorption

### 3.1 Gas Adsorption

Gas adsorption is a phenomenon in which the gaseous molecules attach on the exposed solid surface by using surface forces. Adsorbed molecules are known as the adsorbates while a solid which adsorbs them is called an adsorbent. With physical forces such as van der Waals forces and electrostatic forces, the phenomenon is known as "physical adsorption". While the use of chemical bonds to hold gaseous molecules on the surface is called "Chemisorption" [27].

With utilization of surface forces, an adsorbent ought to be porous particles in order to provide large specific surface area. In addition, utilization of pore surface or internal surfaces depends on the pore size with respect to the molecular size of the adsorbate. In other words, the adsorbate molecules are able to diffuse in a pore which is large than the molecular size. Therefore pore size distribution of an adsorbent is one of characteristics of an adsorbent. Activated carbons, for instance, provide a wide range of pore size distribution [27]. While molecular sieve

adsorbents such as zeolites and carbon molecular sieve (CMS), have unique and narrow pore size distribution, respectively [4].

In general, both specific surface area and pore size distribution of an adsorbent are determined from gaseous the equilibrium adsorption of gaseous nitrogen at temperature of 77 K or the BET method [4]. The specific surface area corresponding to the nitrogen adsorption, which is known as BET surface area, can be obtained with an additional assumption of monolayer or multilayer adsorption. While the resulting pore size distribution is usually in a range less than 1,000 Å. Alternatively, the pore size distribution can be measured by mercury displacement. However, the method is limited at a range of pore sizes below 10,000 Å.

### 3.2 Adsorption Isotherms

In general, an adsorption equilibrium depends on a pair of an adsorbent and an adsorbate, pressure, temperature and concentration of the adsorbate in fluid. For a given pair of an adsorbent and an adsorbate, an expression of the gas adsorption equilibrium is written conventionally for an isothermal system or for an isobaric system. The former is known as an isotherm equation, while the latter is called an isobar equation. The isotherm equation is commonly employed in the field of adsorption.

### 3.2.1 Linear Isotherms

For adsorption on a uniform surface with low amount adsorbed, each adsorbed molecule hardly interacts one another. The amount adsorbed per unit mass of adsorbent is proportional to concentration of the adsorbate. Thus, the isotherm of gas adsorption can be written as:

$$q_i = K_i P_i = P K_i y_i \quad (3.1)$$

$K_i$  is adsorption equilibrium constant for component  $i$ . Since equation 3.1 is analogous Henry's law of dilute solution, the constant is called adsorption Henry's constant, and this equation is valid for dilute solution as well.

Since the adsorption is an exothermic phenomenon, the equilibrium constant decrease as an increase in temperature. It has been found the relationship between the adsorption equilibrium constant (or the adsorption Henry's constant) and heat of adsorption corresponds to van't Hoff equation, which is expressed as:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (3.2)$$

If the heat of adsorption is independent of temperatures equation 3.2 can be integrated and is yielded as:

$$\ln K = -\frac{\Delta H_{ads}}{RT} + C$$

On the other hand, the heat of adsorption can be determined from the slope of the plot of  $\ln K$  versus reciprocal temperature [27].

### 3.2.2 Nonlinear Isotherms

When a large amount of adsorbate molecules is adsorbed on an adsorbent surface, the isotherm tends to be nonlinear. With an increase in the partial pressure of the adsorbate, the amount adsorbed usually approaches a certain value which represents the total amount adsorbed on the surface or the monolayer adsorbed amount. Under the circumstances, the amount adsorbed is limited of this value which is known as the saturated value. Otherwise, the adsorbate can be adsorbed without upperbound or saturation. This type of adsorption may be called multilayer adsorption.

- Saturated Isotherms

As adsorption is restricted to an adsorbent surface only, the adsorbed amount of an adsorbate is limited to the total accessible surface area. Therefore, the surface is covered with a single layer of adsorbate molecules leading to saturation of adsorption. The well known expression of this isotherm is Langmuir's isotherm, which can be written as

$$\frac{q_i}{q_{s,i}} = \frac{K_L P_i}{1 + K_L P_i} \quad (3.3)$$

As an increase in the partial pressure of an adsorbate  $i$ , the amount adsorbed approaches the saturation amount,  $q_{s,i}$ , which corresponds to the total surface area for adsorption of adsorbate  $i$ .

- Unsaturated Isotherms

When an adsorbate molecule can be adsorbed either on an adsorbent surface or on the adsorbed molecules upon the surface, saturation of adsorption never occurs with an increase in the partial pressure of the adsorbate. An expression of this isotherm can be written as

$$q_i = K_a P_i^{1/n} \quad (3.4)$$

Parameter  $n$  is a constant which is not unity. If the parameter  $n$  is greater than unity, equation 3.4 is known as Freundlich isotherm which is an empirical expression. Although the isotherm provides a similar equation curve to that of Langmuir's isotherm, the amount adsorbed is not limited. In the case of that the parameter  $n$  becomes less than unity, equation 3.4 corresponds to isotherm type III according to the BDDT classification [27]. However, this isotherm has rarely been found.

### 3.3 Isotherm Measurements

Gas adsorption equilibrium data can be obtained by direct measurement amounts of adsorbate in both gas and adsorbed phases after achievement of the equilibrium. This measurement is appropriate for a system of concentrated solution. For a dilute solution, the adsorption equilibrium constant, on the other hand, is measured more conveniently than either the amounts adsorbed on the surface or the amounts remained in the gas phase. This method may be called as "indirect

measurement”.

### 3.3.1 Direct Measurements

In order to accelerate an adsorption system to reach equilibrium, a certain amount of adsorbents has to be placed under vacuum and pure adsorbate gas is fed into the system of which the volume, as well as temperature, is controlled. The remaining amount of the adsorbate can be determined from an incremental pressure of the system. The amounts of adsorbated is, therefore, a difference of the amounts of adsorbate between the incremental feed amounts into the system and the corresponding incremental amounts remained in the system. When only the amounts remained is measured , the measurement is know as “volumetric method” The BET adsorption is based on the volumetric method [4]. When a change in the gained weight of the adsorbent is measured instead, the unadsorbed amount is a deduction of the amounts adsorbed from the amounts fed. This method is known as “gravimetric method” [4].

Without vacuum condition, the adsorption equilibrium can be obtained from breakthrough data of steadily continuous feed of a given concentration of adsorbate and a given temperature. However, the breakthrough results must be verified whether the adsorption system reaches equilibrium or steady state. In order to achieve adsorption equilibrium, the feed rate has to be sufficiently slow.

### 3.3.2 Indirect Measurements

When a gaseous mixture contains a small amount of adsorbate, either the volumetric method or the gravimetric method may not provide reliable adsorption equilibrium results depending upon the accuracy of analytical instruments, such as pressure gauge and micro balances. Although breakthrough data can be obtained from steady measurement, it requires a large amount of dilute gas and a long period of each measurement. Under the circumstances, Chromatographic method is appropriate for measurement of the equilibrium constant. In addition, it requires a small amount of dilute gaseous mixture and provides quite reliable results within a short period [28]. With chromatographic conditions, a sufficiently small amount of adsorbate or mixture of adsorbate is injected into the carrier gas stream as a pulse fashion. Figure 3.1 illustrated a typical chromatogram of a pulse injection. Breakthrough data of the pulse feed is record with respect to time. Subsequently, the breakthrough pulses are employed to determine weighted mean residence time,  $t_R$ , in the adsorption region with the first absolute moment which is

$$t_R = \frac{\int_0^{\infty} c(t)t dt}{\int_0^{\infty} c(t) dt}$$

$$\approx \frac{\sum t_i c_i \Delta t_i}{\sum c_i \Delta t_i}$$

The mean residence time relates to the adsorption equilibrium constant, configuration of the packed bed and the operating conditions as follow.

$$t_R = \frac{L}{v} \left( 1 + \left( \frac{1-\epsilon}{\epsilon} \right) K_H \right) \quad (3.5)$$

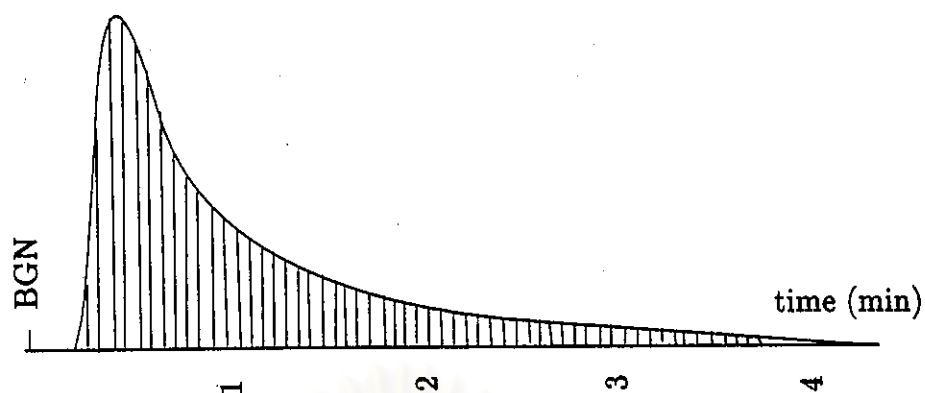


Figure 3.1: Typical chromatogram of chromatographic experiment

### 3.4 Adsorption Kinetics

For adsorption on a single adsorbent, an adsorbate molecule in bulk gas has to travel across gas film surrounding the adsorbent particle and subsequently travel through stagnant gas containing in pore volume of the adsorbent in order to reach gas-adsorbed phase interface, as illustrated in Figure 3.2. When the bulk gas is set in motion, the gas film can move slowly corresponding to laminar flow. Thus, the adsorbate molecule can transfer across the film with diffusion only, namely film diffusion. In the pore volume, since gas can not flow, the adsorbate has to diffuse through the stagnant gas within a restricted space. This phenomenon is called pore diffusion. At the gas adsorbed phase interface, the adsorbate is adsorbed and is considered as adsorption equilibrium. In the adsorbed phase, the adsorbed molecule does not move further because of pure adsorbate on the surface. Consequently, the mechanism of adsorption can be divided into 2 consecutive steps, i.e. the film diffusion and the pore diffusion, of which the slower diffusion becomes



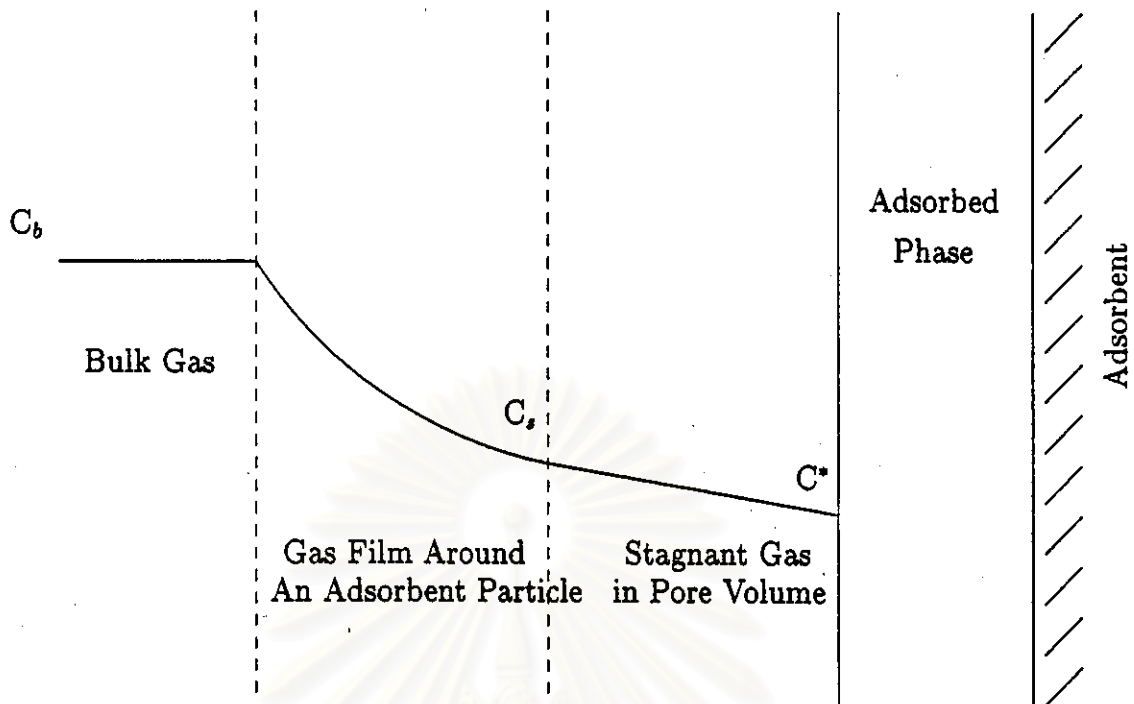


Figure 3.2: Adsorption Kinetics

the rate of adsorption

### 3.4.1 Film Diffusion Control

In practice, the rate of adsorption, which is the rate of mass transfer across the film can be expressed in term of a film mass transfer coefficient,  $k_f$ , as follow:

$$R_{ads} = (K_f a) \frac{1}{\rho_s} \left( \frac{\epsilon}{1 - \epsilon} \right) (c_b - c_s) \quad (3.6)$$

For spherical adsorbents, the interfacial area per unit volume,  $a$ , equals to  $\frac{6}{D_p}$ . The film mass transfer coefficient can be determined from an appropriate correlation of Sherwood number (Sh) with Reynold number (Re) and Schmidt number (Sc) such as:

Marshall equation [27] for a single adsorbent:

$$Sh = 2.0 + 0.6Sc^{1/3}Re^{1/2} \quad (3.7)$$

Wakao and Funazki [27] for a packed bed of adsorbents:

$$Sh = 2.0 + 1.1Sc^{1/3}Re^{0.6} \quad 3 < Re < 10^4 \quad (3.8)$$

### 3.4.2 Pore Diffusion Control

Diffusion within pores occurs with several types of diffusion depending upon pore diameters, characteristic feature of pores, and mean free path of adsorbate molecules. When the mean free path becomes greater than pore diameters, the diffusion obeys Knudsen diffusion and Knudsen diffusivity can be estimated by an expression given below:

$$D_k = 9700r \left( \frac{T}{M} \right)^2 \quad (3.9)$$

Other wise, the diffusion occurs as molecular diffusion corresponding to Fick's law of diffusion. In the circumstance, the diffusivity can be estimated by equation [29] below.

$$D_m = \frac{2.745 \times 10^{-4}}{p} \left( \frac{T}{\sqrt{T_{cA}T_{cB}}} \right)^{1.823} (p_{cA}p_{cB})^{1/3} (T_{cA}T_{cB})^{5/12} (1/M_A + 1/M_B)^{1/2} \quad (3.10)$$

Since the pores are rarely straight, the effective pore diffusivity depends on the corresponding diffusivity and tortousity factor, as the expression given below:

$$D_p = \frac{D}{\tau} \quad (3.11)$$

However, an adsorbate molecule need not diffuse to the end of a pore for adsorption.

Alternatively, the rate of pore diffusion can conveniently be expressed in term of pore mass transfer coefficient,  $k_p$ , as given below:

$$R_{ads} = k_p a_s \frac{1}{\rho_s} \left( \frac{\epsilon}{1 - \epsilon} \right) (c_s - c^*) \quad (3.12)$$

Since the adsorbate concentration at the external surface of adsorbent pellets is hardly obtained, the rate of adsorption can be expressed in term overall mass transfer coefficient,  $k_0$ , corresponding to combination of equation 3.6 and equation 3.12

$$R_{ads} = k_0 (c_b - c^*) \quad (3.13)$$

where

$$k_0 = \rho_s \left( \frac{1 - \epsilon}{\epsilon} \right) \left( \frac{1}{k_f a} + \frac{1}{k_p a_s} \right)^{-1} \quad (3.14)$$

### 3.5 Axial Dispersion

Besides adsorption equilibria and adsorption kinetics, gas separation performance also depends on a degree of diffusion in the fluid flow direction, namely axial

dispersion. The separation efficiency is reduced by the axial dispersion. In comparison between the dispersion and convection, the relative important of the axial mass transfer can be indicated by the Peclet number, i.e. the mass transfer is dominated by the axial dispersion for a small value of the Peclet number. With the second central moment of a pulse chromatogram, which is defined as:

$$\begin{aligned}\sigma^2 &= \frac{\int_0^{\infty} c(t)(t-t_R)^2 dt}{\int_0^{\infty} c(t) dt} \\ &\simeq \frac{\sum c_i(t_i-t_R)^2 \Delta t}{\sum c_i \Delta t}\end{aligned}$$

Both the overall mass transfer coefficient and the axial dispersion can be determined from the equation below:

$$\frac{\sigma^2}{2t_R^2} = \frac{D_L}{vL} + \frac{v}{L} \left( \frac{\epsilon}{1-\epsilon} \right) \left( \frac{1}{k_0 K_H} \right) \left( 1 + \frac{\epsilon}{(1-\epsilon)K_H} \right)^{-2} \quad (3.15)$$

Subsequently, the pore mass transfer coefficient can be determined from equation 3.15.

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